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Change Of Attorney Or Agent's Address In Application (37 CFR 1.8(a))	Docket No. 665-P-5
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In Application Of: **Gerald J. Grott**

Application No. 10/706,341	Filing Date November 11, 2003	Examiner Jeffrey L. Gellner	Group Art Unit 3643
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Invention:
METHODS OF UTILIZING WASTE WATER PRODUCED BY WATER PURIFICATION PROCESSING

COMMISSIONER FOR PATENTS


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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Before the Board of Patent Appeals and Interferences

re:

Applicant : Gerald J Grott
Serial Number: 10/706,341
Filed : November 11, 2003
For : METHODS OF UTILIZING
WASTE WATER PRODUCED
BY WATER PURIFICATION
PROCESSING

Primary Examiner
Jeffrey L. Gellner

Art Unit 3643

BRIEF FOR APPLICANT

This an appeal under 37 CFR §§41.30 et seq. from the Final Rejection of all claims then in the application, Claim 4-6. This Brief is submitted in compliance with 37 CFR §41.37.

THE REAL PARTY IN INTEREST

The real party in interest is the appellant, Applicant-Inventor, Gerald J. Grott.

RELATED APPEALS AND INTERFERENCES

There are no other prior or pending appeals or interferences known to appellant or his undersigned attorney which may be related to, directly affect or be directly affected, by or have a bearing on the Board's decision in the present appeal.

STATUS OF THE CLAIMS

Originally filed Claims 1-3 and 7-14 have been cancelled.

Claims 4-6, all of the claims in the case were finally rejected by the Primary Examiner.

STATUS OF AMENDMENTS

There have been no amendments presented which have not been entered in the case.

SUMMARY OF THE CLAIMED SUBJECT MATTER

CLAIM 4

Specification (See Page 16, line 12 – Page 19, line 8; Example 2, Figs 1-5)

Contaminated water (e.g., agricultural runoff) containing salts of sodium, calcium and magnesium, especially their chlorides, sulfates and carbonates, are processed to produce a first effluent “clean” water stream and a second effluent “waste” water stream.

The first or “clean” water stream has a higher sodium content than the contaminated water, i.e., increased sodium in comparison to the original contaminated water. The second or “waste” water stream has more than 0.15% of the salts.

The “clean” water stream is analyzed to determine if its sodium content is higher than that necessary for potable use. If so, it is used in a cooling tower to dissipate heat.

Claims 5-6

In one preferred embodiment of the method, the contaminated water is first processed by "water softening," e.g., removal of scale forming materials such as calcium or magnesium salts, especially their carbonates. (Claim 5) In other preferred embodiments, the contaminated water is first processed by ion-exchange, precipitation, membrane softening or electrolysis. (Claim 6)

THE GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

Claims 4-6, all of the claims in the case, were finally rejected under 35 U.S.C. §103(a) as unpatentable over McManus, in view of Thorburg in further view of Mukhopadhyay.

ARGUMENT

GROUPING OF THE CLAIMS

Applicant will argue the patentability of independent Claim 4. The dependent Claims 5 and 6 will stand according to the Board's decision on Claim 4.

I. The Examiner erred in combining the references.

Where the Examiner relies upon a combination of prior art references, he bears the burden of showing some teaching or suggestion in these references that supports their use in combination. *Ashland Oil, Inc. v. Delta Resins & Refractories, Inc.*, 776 F.2d 281, 293, 297; 227 USPQ 657 (Fed.Cir. 1985). The Examiner has not identified the particular teachings of the McManus or Thorburg references which “would have” (§103) motivated the person of ordinary skill to combine the teachings of these references to make the combination of steps claimed by Applicant.

Instead of pointing to any such teaching or suggestion, the Examiner airily dismisses Applicant’s argument by stating that the “references used in the rejections to be combinable because they all deal with water use and purification.” (Final Rejection, page 4.) This falls far short of the standard for making a *prima facie* case of obviousness. *In re Dembiczak*, 175 F.3d 994, 1000, 50 USPQ2d 1614 (Fed.Cir. 1999)(broad conclusory statements are not evidence)(modified on other grounds 203 F.3d at 1316).

II. The references teach away from the claimed method.

McManus, the primary reference, teaches the use of agricultural wastewater produced from crop irrigation in a cooling tower. A pilot-scale plant (fig. 4, p. 155) was constructed consisting of an electric heater to produce simulated hot water continuously fed in one pass

through the shell side of a tube/shell heat exchanger. The wastewater from a cooling tower made four passes through the heat exchanger, then was recycled to the top of a cooling tower. A side-stream of the wastewater (taken before the cooling tower) was mixed with makeup wastewater. This makeup-recycle mixture was continuously treated with lime, soda ash and a polymer coagulant in a treatment vessel and then sent to a thickener vessel. The underflow sludge from the thickener was discarded to an evaporation pond. The supernatant water recovered from the thickener was recycled to the treatment vessel and the treated supernatant-makeup mixture was then sent to the cooling tower sump. The coolant stream from the cooling tower was acidified with sulfuric acid.

The selected treatment process to control the circulating water chemistry was lime/soda softening. Chemical constituents to be controlled through treatment were calcium, magnesium and silica. (McManus, p. 441) (emphasis added)

The operation of this pilot plant proved effective at high cycles of concentration which achieved the overall objectives of reducing makeup requirements and waste volumes for ultimate disposal. For the particular makeup source evaluated, conventional lime/soda softening with polymer coagulation proved to be effective even at 30 cycles of concentration.

These results are significant because they demonstrate that it is feasible to operate recirculated cooling system at high cycles of concentration and with agricultural waste water makeup without sophisticated treatment such as ion exchange or reverse osmosis. (emphasis added)

Scale components of concern include calcium carbonate, magnesium silicate and calcium sulfate complexes. (McManus, p. 445)

Thus, it is seen that **McManus** is not at all concerned with the sodium content of either the original raw wastewater or the sodium content of his recirculating stream to the cooling tower. A person of ordinary skill in the art would find no hint or suggestion of a process such as defined

by Applicant's Claim 4, based on sodium content of either the wastewater or the cooling tower water and would be directed away from use of "ion exchange."

Thorburg disclosed a continuous process in which raw water ("salt-containing impure water") (Col. 1, line 12) is passed upwardly through a downwardly moving bed of a weak anion exchange resin in the form $R-HCO_3$, forming the respective carbonates of the raw water components (e.g., sodium carbonate). This "first effluent" is then treated countercurrently with a weak acid cation exchange resin in the form $R'H$.

The released hydrogen reacts with the bicarbonate present thereby leaving pure water and carbon dioxide...The resin leaves the bottom of the dealcalization unit in the metal form $R'-Me$ (containing calcium, magnesium sodium, etc.). .. (Column 2, lines 32-36)(emphasis added).

Thus, the first effluent of **Thorberg** contains all of the sodium in the raw water (as sodium carbonate) and the second effluent is "pure water" (containing no sodium) with all of the sodium content exiting the treatment column as $R'Na$. This is expressly contrary to Applicant's claimed method where the "clean water" contains "increased sodium so as to have more sodium than the contaminated water" (Claim 4) and nowhere does **Thorberg** have "a salt content too high for potable use" (Claim 4) – again teaching squarely away from Claim 4 and squarely away from the combination of **Thorberg** (ion exchange) with **McManus** which "would have" (§103) led the worker of ordinary skill to use conventional water softening of a sidestream-makeup water stream, rather than ion exchange of the entire impure water input.


CONCLUSION

There is nothing in either reference which would suggest the combination proposed by the Examiner. Each of the applied references teaches away from the proposed combination.

The Board is respectfully requested to reverse the Final Rejection of Claims 4-6 and remand the application to the Examiner for further processing and a Notice of Allowance.

A Petition for Extension of Time to file the Appeal Brief is filed concurrently herewith, along a check in payment of the extension fee of \$60.00 and the Appeal Brief fee for a small entity of \$250.00.

Respectfully submitted,


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CLAIMS APPENDIX

Claim 4: A method of using an aqueous effluent comprising the steps of:

collecting water contaminated by the salts of Na, Ca, Mg, Cl, SO₄, or CO₃;

processing the contaminated water to produce a first effluent of clean water and a second effluent of waste water,

the clean water having increased sodium so as to have more sodium than the contaminated water and having a salt content too high for potable use,

and

a second effluent of waste water having 1.5% or more by weight of the salts of Na, Ca, Mg, Cl, SO₄, or CO₃ or combinations thereof and a greater salt content than the clean water;

analyzing the clean water to determine if its sodium content is too high for potable use,

and

using the clean water within a cooling tower to dissipate heat if it has been determined that the clean water's sodium content is too high for potable use.

Claim 5: The method of using an aqueous effluent of Claim 4 wherein the step of processing the contaminated water includes the step of water softening.

Claim 6: The method of using an aqueous effluent of Claim 5 wherein the step of processing the contaminated water is by ion-exchange, precipitation, membrane softening or electrolysis.

EVIDENCE APPENDIX

No evidence except the references discussed above was entered by either Applicant or the Examiner. These references were entered by the Examiner at page 2 of the Office Action mailed 10/29/2006. Copies of these references are appended hereto at pages 12 and 13 of this Brief.

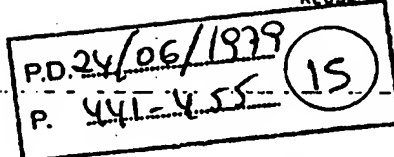
RELATED PROCEEDINGS APPENDIX

None.

The McManus Reference

XP-001030054

REUSE OF AGRICULTURAL WASTEWATER FOR POWER PLANT COOLING
ONE-YEAR PILOT PLANT EXPERIENCE



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Accelerating energy demands and diminishing supplies of fresh water for cooling, are forcing the power industry to seek new sources of cooling water. One potential source for cooling water is the agricultural wastewater produced from crop irrigation. In many arid sections of the United States, water is withdrawn from freshwater sources and applied to cropland via flooding and/or spray techniques. Excess water percolates through the ground and discharges as waste water to a receiving stream. This paper presents the results of a one-year pilot plant study to evaluate the use of agricultural wastewater in an open recirculated cooling system with zero effluent discharge. The objectives of the program were to determine the feasibility of this cooling system from the standpoint of (1) makeup water requirements, (2) scaling potential and (3) heat transfer impacts of the selected treatment scheme.

PILOT PLANT DESIGN

The pilot plant was sized to simulate the cooling system required for a 1,000 MW electric generating facility. The test facility shown schematically in Figure 1 models the treatment system, cooling tower, condenser, the heat load to the condenser and ultimate disposal of solids. Flow rates were sized at approximately one tenth of one percent of a full-scale facility. This represents a recirculating cooling flow rate of 500 gallons a minute (gpm) with an evaporation rate of ten gpm. The condenser was constructed with titanium tubes and an aluminum bronze tube sheet. Design temperature range for the four pass circulating water was 90° to 120°F while the shell side was a single pass with an inlet temperature range of 130° to 150°F. The shell side heat source was an electric hot water heater with a closed loop recirculation rate of 500 gpm. The makeup water was pumped from an agricultural outfall drain to a 1,000 gallon holding tank. Makeup flow was controlled by a level system in the cooling tower basin.

The selected treatment process to control the circulating water chemistry was lime/soda softening. Chemical constituents to be controlled through treatment were calcium, magnesium and silica. To achieve zero effluent, system blowdowns, either through direct blowdown of circulating water or treatment plant sludges, were disposed of via solar evaporation. The treatment system was designed for a recirculating cooling system operated at 15 cycles of concentration to minimize blowdowns.

PRELIMINARY INVESTIGATION

The first phase of the program was to evaluate three treatment modes:

1. Sidestream treatment
2. Separate makeup and sidestream treatment
3. Combined makeup and sidestream treatment

McManus

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These treatment modes were operated under the common conditions of 15 cycles of concentration (based on chlorides) with a circulating water total hardness of 700 mg/l as CaCO_3 . The performance criteria of concern were:

1. Heat transfer efficiency
2. Chemical costs
3. Operating flexibility

Each treatment mode was operated for a period of 6-8 weeks. At the end of each test period, the condenser tubes were physically inspected for scale buildup.

Sidestream Treatment

Figure 2 presents the process flow schematic for sidestream treatment at 15 cycles of concentration. Makeup water is discharged directly into the cooling tower basin. Water for sidestream treatment and blowdown is drawn from the hot side of the condenser. The warmer temperatures enhance calcium carbonate precipitation. The combined sidestream and thickener supernatant flows are treated with lime and soda ash for softening. Ferric chloride and polymer were added to enhance suspended solids removal. Sodium hypochlorite and sulfuric acid are fed into the circulating water to control biofouling and to adjust pH, respectively. Makeup, sidestream effluent and circulating water characterizations are presented in Table 1. This treatment scheme minimizes equipment requirements.

Separate Makeup and Sidestream Treatment

The process flow schematic for separate makeup and sidestream treatment is illustrated in Figure 3. Treatment of makeup and thickener supernatant consists of lime softening with ferric chloride and polymer coagulation. Sidestream treatment consists of lime/soda softening with ferric chloride and polymer coagulation. Table 2 presents the characterization of the makeup, the two treated effluents and the circulating water. This scheme maximizes control of circulating water chemistry.

Combined Makeup and Sidestream Treatment

Figure 4 presents the flow schematic for combined makeup and sidestream treatment. Makeup, sidestream and thickener supernatant flows are mixed and treated via lime/soda softening with ferric chloride and polymer coagulation. As with the other two systems, sodium hypochlorite is added for biofouling control while sulfuric acid is added to the circulating water for pH control. Characterization of the makeup, treated effluent and circulating water are presented in Table 3. This system incorporates the advantages of the other two; one treatment system and satisfactory control of circulating water chemistry.

Performance Evaluation

One of the prime criterion for performance evaluation of the cooling system is heat transfer efficiency. Reduction in heat transfer efficiency is caused primarily by the scaling of the condenser tubes.

This criterion was evaluated via continuous monitoring of heat transfer using the flow rates and inlet and outlet temperatures of the tube side and shell side recirculating waters. After each operating mode, the system was shut down, and the condenser was physically inspected. Heat transfer monitoring indicated virtually no degradation. Physical inspection confirmed that no significant scale deposition was present.

Circulating water chemistry was comparable for all three treatment schemes. Sidestream treatment exhibited the highest calcium to magnesium ratio while combined treatment exhibited the lowest. Silica control was excellent for all three systems, with separate treatment proving most effective. Table 4 presents the chemical usage and cost per thousand gallons of makeup for the three treatment schemes. This evaluation demonstrates that sidestream treatment followed by combined treatment is more cost-effective than separate treatment. The relatively low usage of ferric chloride and polymer for sidestream treatment acts favorably on its total cost. Because the addition of these two coagulants was not optimized during this phase of testing, the total cost figures are artificially inflated for the separate and combined treatment schemes. Normalized costs which consider usage of only lime, soda ash and sulfuric acid are more germane at this point in the investigation. Combined treatment is thus demonstrated to be slightly more cost-effective primarily because alkalinity control of the makeup to the cooling system is optimized. Thus, there is a reduction in sulfuric acid usage.

From a process operating standpoint, separate and combined treatment schemes were superior to sidestream treatment because the chemical quality of the makeup can be altered to facilitate the desired chemistry of the circulating water system. With no makeup treatment, the cooling tower chemistry is more difficult to control due to the potential fluctuations in the quality of the makeup water. Separate treatment does offer slightly more operating flexibility than combined treatment. However, the additional capital investment and operating expense for the multiple equipment system outweigh the benefits of flexibility.

Based on the results of the preliminary investigation, combined makeup and sidestream treatment was the selected process for optimization. The next section discusses the five-month optimization program.

SYSTEM OPTIMIZATION

The objective of the second phase of the program was to evaluate the cooling system under more severe operating conditions using the selected treatment system from Phase I. Two modes of operation were evaluated. For the first mode, the circulating water was operated at 15 cycles of concentration with a calcium concentration of 900 mg/l as CaCO_3 . For the second mode, the calcium concentration was maintained at 900 mg/l, however, the cycles of concentration were increased to 30. Combined treatment as illustrated in Figure 4 was used during this phase of testing. The minor adjustments to this scheme included (1) eliminating ferric chloride as a coagulant, (2) decreasing in the sidestream flow rate from approximately eight to four gpm, and (3) decreasing the volume of water discharged with the sludge in order to increase the cycles of concentration to 30.

The first mode will be identified as 15 cycles with high calcium while the second mode will be identified as 30 cycles with high calcium.

Fifteen Cycles with High Calcium

To achieve higher calcium concentrations in the circulating water, the volume of sidestream flow to be treated was reduced. Table 5 presents the characterization of the makeup treated effluent and circulating water. With the exception of calcium and magnesium, the circulating water chemistry for this program compares well with the results presented in Table 3. By reducing the sidestream flow, the calcium and total hardness concentrations in the circulating water increased to the levels of 900 and 1,884 mg/l as CaCO_3 , respectively. Under these operating conditions, no decrease in heat transfer efficiency occurred. A physical inspection at the termination of this mode confirmed that no significant scale was present in the heat exchanger tubes.

Thirty Cycles With High Calcium

To achieve 30 cycles of concentration with the pilot plant, it was necessary to minimize blowdown from the system. This was accomplished by increasing the volume of supernatant recovered in the thickener and eliminating direct blowdown from the hot side of the condenser to the evaporation basin. Characterizations of the makeup, treated effluent and circulating water are presented in Table 6. As expected, the circulating water under 30 cycles exhibits approximately double the concentrations of chlorides, sodium, sulfate and dissolved solids as exhibited at 15 cycles of concentration. The calcium, magnesium, silica and suspended solids concentrations were maintained at levels comparable to 15 cycles. No adverse impact on heat transfer efficiency occurred during the two-month study at 30 cycles of concentration. Physical inspection of the heat exchanger substantiated these findings.

Discussion of System Optimization

Because no heat transfer reduction occurred under these two modes, it appears that it is possible to operate at both higher levels of calcium and cycles of concentration than originally estimated during the preliminary investigation. Table 7 presents the chemical usage and the cost data for the three operating modes employing combined treatment. The results indicate that operation at 15 cycles of concentration and high calcium represents a significant savings in the usage of lime, soda ash and sulfuric acid when compared to low calcium operation. The chemical cost at 15 cycles and high calcium is further reduced because the ferric chloride addition was eliminated and polymer addition was reduced by half without any significant impact on the suspended solids concentration in the treated effluent. In comparing high calcium systems at 15 and 30 cycles, it is apparent that the chemical usage of lime and soda ash increased markedly, but only increased slightly for sulfuric acid. The lime and soda ash dosages are higher because the treatment efficiency for calcium must be increased by approximately 30% at 30 cycles of concentration in order to maintain 900 mg/l of calcium. The increase in sulfuric acid usage is not considered significant.

Although the chemical requirements at 30 cycles of concentration exceeded the usage at 15 cycles, the benefit of the reduced blowdown has a significant impact on the overall cost. The blowdown at 30 cycles of concentration is half that at 15 and, thus, reduces the required evaporation basin capacity by approximately 50 percent. This represents a significant capital cost saving and should outweigh the added chemical cost of operating at 30 cycles.

DISCUSSION OF RESULTS

The operation of this pilot plant proved effective at high cycles of concentration which achieved the overall objectives of reducing makeup requirements and waste volumes for ultimate disposal. For the particular makeup source evaluated, conventional lime/soda softening with polymer coagulation proved to be effective treatment even at 30 cycles of concentration. At 30 cycles of concentration and a TDS of 46,140 mg/l, there was no measurable impact on heat transfer efficiency, which was maintained at approximately 600 Btu/hr-ft² of throughout the testing program. These results are significant because they demonstrate that it is feasible to operate recirculated cooling system at high cycles of concentration and with agricultural wastewater makeup without sophisticated treatment such as ion exchange or reverse osmosis. It is also important to note that under the conditions tested, neither filtration of treated effluent nor the addition of scale inhibitors to the circulating water was required. Sulfuric acid addition for pH control and, ultimately, calcium carbonate precipitation, proved effective without jeopardizing system operation because of calcium sulfate scaling. The use of sulfuric acid for pH control is desirable because it is less expensive than hydrochloric acid.

Circulating Water Chemistry

In high cycle recirculating cooling water systems, the prime concern is to prevent scaling from occurring in the condenser, a condition that reduces heat transfer efficiency. Scale components of concern include calcium carbonate, magnesium silicate and calcium sulfate complexes. It is common practice to control calcium carbonate precipitation via acid addition. This was accomplished in the pilot study by using sulfuric acid. Several investigators^{1,2,3} have proposed recommended operating limits for high cycle recirculated cooling water. Frazer¹ states that (1) calcium sulfate precipitation will not occur if the calcium hardness does not exceed 1,000 mg/l and the temperature is <170°F without regard to sulfate concentration and (2) silica scale will not occur if the concentration is <150 mg/l. Crits, et al² propose limits of (1) pH, 7.5-8.5, (2) silica, 150-200 mg/l, (3) a magnesium silicate product of 6.0×10^4 and (4) a calcium sulfate product of $2.5-8.0 \times 10^6$. In the experimental work of Klen and Johnson,³ the authors predict that precipitation of calcium sulfate will not occur if the calcium concentration is maintained at <800 mg/l as CaCO₃ independent of sulfate concentration in the range of 6,000-18,000 mg/l as SO₄. Table 8 presents these recommended criteria and the pilot plant operating data at high calcium concentration for 15 and 30 cycles. When the operating data are compared to the criteria, the results indicate that there should be no scaling of magnesium silicate complexes; however, it is possible that calcium sulfate scale will occur in the system.

Magnesium silicate complexes prove to be no problem because lime soda softening effectively removed the silica. The average silica concentration of the makeup water was 20 mg/l. Without treatment, the silica concentrations in the circulating water at 15 and 30 cycles would have increased to 330 and 660 mg/l, respectively. Due to the high calcium and magnesium to silica ratios in the makeup water, treatment for silica was extremely effective. The controlling parameter for softening was calcium, and therefore the magnesium concentrations in the treated effluent were well controlled.

Although not intended as a detailed discussion of calcium sulfate chemistry, it is important to discuss the findings of this pilot plant study because the results support the contention that high cycles of concentration can be achieved in recirculating cooling systems without significant restriction due to calcium sulfate precipitation. In low TDS solutions (<2,000 mg/l), the simple solubility product for calcium sulfate is 2.33×10^{-6} as CaCO_3 . As the TDS of a solution increases, the ionic strength impacts on the solubility product of calcium sulfate. Stumm and Morgan⁴ report that the solubility of a salt in a high TDS solution is not governed by its simple solubility product because other equilibria occur in the solution. Cations can react with water to form hydroxo complexes, while anions undergo acid-base reactions. In addition, the cations and anions of the various salts in solutions can form complexes with each other. These side reactions will tend to increase the solubility of calcium sulfate in the recirculating water. Both Klen and Johnson¹ and Skillman, et al.,⁵ report that solubility of calcium sulfate is significantly impacted by the ionic strength of the solution. The ionic strength decreases the ion activity coefficients for calcium and sulfate which in effect reduces the concentration of active ion species available to form calcium sulfate complexes, and, thus, subsequently increases the solubility. Ionic strength can be calculated by the following equation which is presented by Stumm and Morgan:⁴

$$I = 1/2 \sum C_i Z_i^2$$

Where: I = Ionic Strength

C_i = Concentration of Ion

Z_i = Charge of Ion

Using the above equation and the chemical characterization data presented in Tables 5 and 6, the ionic strengths of the circulating water at 15 and 30 cycles of concentration are calculated to be 0.47 and 0.93, respectively.

In laboratory studies, Skillman, et al.⁵ evaluated calcium sulfate precipitation in varying ionic solutions using standard stock solutions of NaCl , MgCl_2 , Na_2SO_4 and CaCl_2 . This study was performed at 77°F and the results compared to those associated with calcium sulfate solubility in sodium chloride solutions with varying ionic strength performed at 50°F, 95°F, 122°F and 176°F. Based on these studies and the calculated ionic strengths, the predicted maximum calcium concentration without the formation of calcium sulfate

precipitate at 15 and 30 cycles of concentration would be 1,030 and 825 mg/l as CaCO_3 , respectively. The actual operating conditions were 900 mg/l at 15 cycles and 862 mg/l at 30 cycles. The calculations predict that precipitation of calcium sulfate should not occur at 15 cycles of concentration--and that there is a slight potential at 30. The fact that calcium sulfate scaling did not occur under operating conditions at 30 cycles of concentration may be attributed to such factors as velocity through the tubes, which could not be simulated in the pure studies performed by Skillman, et al.

Overall, the results compare well with the predictions of other investigators. The fact that the recirculating cooling water can be operated at high calcium and sulfate concentrations without the occurrence of significant scale deposition is encouraging. Because high cycles of concentration can be maintained using lime/soda softening, the implementation of recirculating cooling water systems employing minimal makeup and blowdown is an economically and technically feasible. Additional studies should be undertaken to expand the practical operating limits of calcium sulfate solubility in both full-scale and pilot plant experimentation.

CONCLUSIONS

The result of this one-year pilot program demonstrate that agricultural wastewater is a feasible source for makeup to a recirculating cooling system. Using combined makeup and sidestream lime/soda softening, the recirculating cooling water can be operated at up to 30 cycles of concentration without significantly reducing heat transfer. Operating at high cycles, significantly reduces makeup requirements and subsequent blowdown which requires ultimate disposal. With the particular makeup water investigated, the primary scaling constituent of concern was calcium sulfate. Levels of 20,000 mg/l of sulfate and 860 mg/l of calcium as CaCO_3 were maintained without significant scale formation. Hopefully, the results of this study will encourage the power industry to seriously consider the use of agricultural wastewater for cooling.

REFERENCES

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2. CRITS, G. J. & GLOVER, G., Cooling Blowdown in Cooling Towers, Water and Wastes Engineering, (April, 1975).
3. KLEN, E. F. & JOHNSON, D. A., Improved Laboratory Method for Predicting Calcium Sulfate Solubility in Zero Blowdown Cooling Tower Systems, Proc. National Association of Corrosion Engineers, Houston, TX (March, 1976).

4. STUMM, WERNER & MORGAN, JAMES, Aquatic Chemistry, Wiley-Interscience A Division of John Wiley & Sons, Inc., New York, NY (1970).
5. SKILLMAN, H. L., MC DONALD, J. P., JR. & STIFF, H. A., JR., A Simple, Accurate, Fast Method for Calculating Calcium Sulfate Solubility in Oil Field Brine, Proc. Spring Meeting of the Southwestern District Division of Production of the American Petroleum Institute, Lubbock, TX (March, 1969).

TABLE 1

Sidestream Treatment

Constituent(1)	Makeup	Sidestream Effluent	Circulating Water
Chloride as Cl	339	5,440	5,550
Calcium as CaCO ₃	330	121	471
Magnesium as CaCO ₃	175	101	295
pH, units	8.0	10.7	8.2
Silica as SiO ₂	22	11	38
Sodium as Na	220	8,660	8,710
Solids-Dissolved	1,681	26,200	26,780
Solids-Suspended	15	26	17
Sulfate as SO ₄	533	11,130	11,510
Flow, gpm	8-13(2)	9.7	500
Flow, (l/s)	(0.50-0.82)	(0.61)	(31.5)
Cycles of Concentration(3)			16.3

(1) All values reported in mg/l unless otherwise specified.

(2) Demand varied with evaporation.

(3) Based on chlorides.

TABLE 2

Separate Makeup and Sidestream Treatment

Constituent(1)	Makeup	Makeup(2) Effluent	Sidestream Effluent	Circulating Water
Chloride as Cl	356	775	5,450	5,520
Calcium as CaCO ₃	335	171	137	394
Magnesium as CaCO ₃	180	163	148	315
pH, Units	8.0	9.5	10.4	8.2
Silica as SiO ₂	23	17	12	31
Sodium as Na	230	1,230	8,650	8,680
Solids-Dissolved	1,766	3,400	24,280	24,480
Solids-Suspended	53	34	29	11
Sulfate as SO ₄	564	1,360	11,140	11,530
Flow, gpm	10-14(3)	11-15	8	500
Flow, (l/s)	(0.63-0.88)	(0.69-0.95)	(0.50)	(31.5)
Cycles of Concn.(4)				15.5

- (1) All values reported in mg/l unless otherwise specified.
 (2) Includes thickener supernatant.
 (3) Demand varied with evaporation.
 (4) Based on chlorides.

TABLE 3

Combined Makeup and Sidestream Treatment

Constituent(1)	Makeup	Treated(2) Makeup	Circulating Water
Chloride as Cl	365	2,550	5,890
Calcium as CaCO ₃	329	120	319
Magnesium as CaCO ₃	189	171	393
pH, units	8.0	10.4	8.1
Silica as SiO ₂	21	18	39
Sodium as Na	238	3,630	8,460
Solids-Dissolved	1,732	11,300	25,930
Solids-Suspended	24	41	12
Sulfate as SO ₄	546	4,540	10,570
Flow, gpm	10-13.5(3)	19-22	500
Flow, (l/s)	(0.63-0.85)	(1.20-1.39)	(31.5)
Cycles of Concentration(4)			16.1

- (1) All values reported in mg/l unless otherwise specified.
 (2) Includes makeup, sidestream and thickener supernatant flows.
 (3) Demand varied with evaporation.
 (4) Based on chlorides.

TABLE 4
Chemical Usage and Cost Comparison

Chemical	Usage in lbs per 1000 Gallons of Makeup			
	Sidestream Treatment		Combined Treatment	
	lbs/1000 gal	(kg/m ³)	lbs/1000 gal	(kg/m ³)
Lime	1.91	(0.229)	3.23	(0.387)
Soda Ash	4.11	(0.492)	3.46	(0.414)
Ferric Chloride	0.15	(0.018)	0.32	(0.038)
Polymer	0.01	(0.001)	0.02	(0.002)
Sodium Hypochlorite	0.08	(0.009)	0.08	(0.009)
Sulfuric Acid	2.05	(0.245)	2.94	(0.352)
Cost, \$/1,000 gal	30.9	(8.16)	35.5	(9.38)
Normalized Cost(2)	27.5	(7.26)	29.2	(7.71)
			32.1	(8.48)
			26.0	(6.87)

(1) Lime - 1.5¢/lb.; Soda Ash - 4.5¢/lb; Ferric Chloride - 5.3¢/lb; Polymer - 2.00¢/lb;
Sodium Hypochlorite (cost based on chlorine) - 6.8¢/lb; Sulfuric Acid - 3.0¢/lb.
Excluding polymer, all prices are FOB United States, based on April 30, 1979 issue of Chemical Marketing Reporter.

(2) Includes only cost for lime, soda ash and sulfuric acid usage.

TABLE 5
Combined Treated (15 Cycles - High Calcium)

Constituent(1)	Makeup	Treated Makeup	Circulating Water
Chloride as Cl	336	1,890	5,480
Calcium as CaCO ₃	330	311	900
Magnesium as CaCO ₃	175	344	984
pH, units	8.0	10.5	8.2
Silica as SiO ₂	22	14	41
Sodium as Na	280	2,510	7,310
Solids-Dissolved	1,646	8,160	23,440
Solids-Suspended	34	58	10
Sulfate as SO ₄	532	3,300	9,350
Flow, gpm	11.4	15.2	500
Flow, (l/s)	(0.72)	(0.96)	(31.5)
Cycles of Concentration			16.3

(1) All values reported in mg/l unless otherwise specified.

TABLE 6
Combined Treated (30 Cycles - High Calcium)

Constituent(1)	Makeup	Treated Makeup	Circulating Water
Chloride as Cl	339	2,820	10,210
Calcium as CaCO ₃	338	230	862
Magnesium as CaCO ₃	172	261	996
pH, units	8.0	10.6	8.1
Silica as SiO ₂	19	11	36
Sodium as Na	286	3,970	14,610
Solids-Dissolved	1,687	12,290	46,140
Solids-Suspended	28	46	15
Sulfate as SO ₄	547	5,140	20,650
Flow, gpm	11.5	15.7	500
Flow, (l/s)	(0.73)	(0.99)	(31.5)
Cycles of Concentration			30.1

(1) All values reported in mg/l unless otherwise specified.

TABLE 7

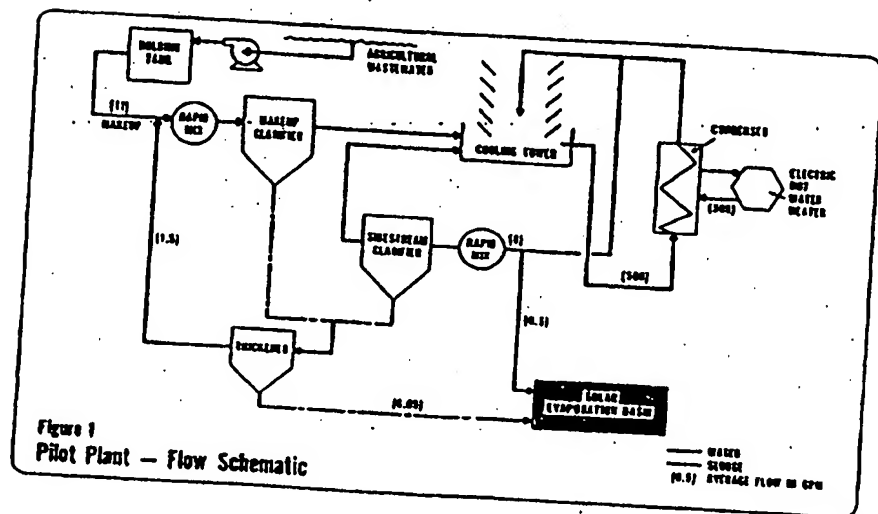
Chemical Usage and Cost Comparison - Combined Treatment

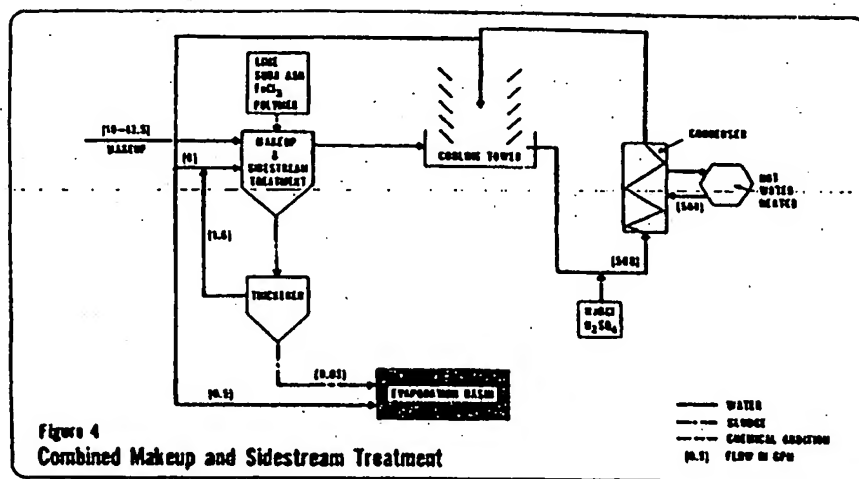
Chemical	Usage in lbs per 1000 Gallons of Makeup					
	15 Cycles - Low Calcium		15 Cycles - High Calcium		30 Cycles - High Calcium	
	lbs/1000 gal	(kg/m ³)	lbs/1000 gal	(kg/m ³)	lbs/1000 gal	(kg/m ³)
Lime	2.83	(0.339)	1.93	(0.231)	2.42	(0.290)
Soda Ash	3.79	(0.454)	1.92	(0.230)	2.48	(0.297)
Ferric Chloride	0.31	(0.037)	--	--	--	--
Polymer	0.02	(0.002)	0.01	(0.001)	0.01	(0.001)
Sodium Hypochlorite	0.08	(0.009)	0.08	(0.009)	0.08	(0.009)
Sulfuric Acid	1.55	(0.186)	0.78	(0.093)	0.91	(0.109)
Cost, \$/1000 gal (¢/m ³)	32.1	(8.48)	16.4	(4.33)	20.1	(5.31)

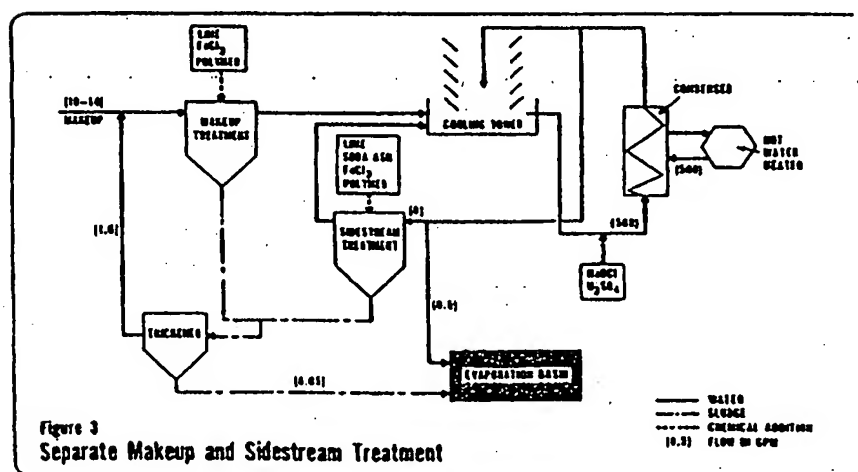
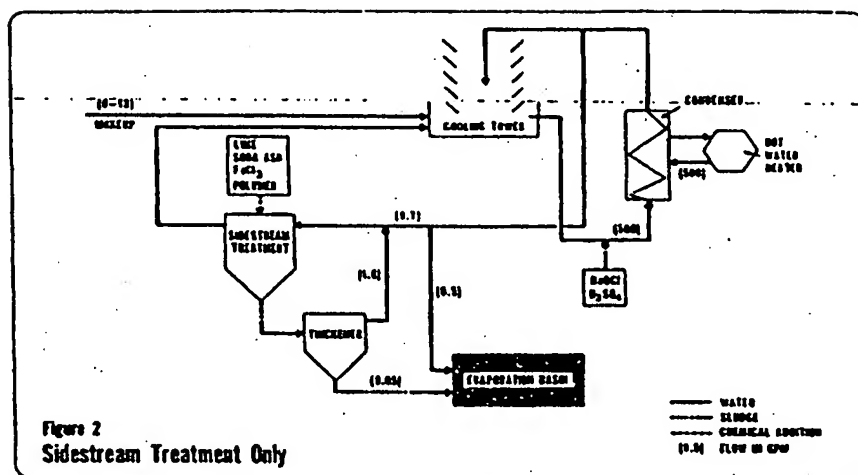
Circulating Water Control Limits

	Recommended Criteria	Reference Source	Combined Treatment Operating Data	
			15 Cycles	30 Cycles
pH, units	7.5-8.5	2	8.2	8.1
Silica as SiO ₂	150-200	1,2	41	36
Mg x SiO ₂	6.0-10 ⁴	2	1.0x10 ⁴	0.9x10 ⁴
Ca x SO ₄ as CaCO ₃	2.5-8.0x10 ⁶	2	6.7x10 ⁶	18.5x10 ⁶
Calcium as CaCO ₃	1000,(800)	1,(3)	900	862
Sulfate as SO ₄	No limit (6-18x10 ³)	(3)	9.3x10 ³	20.6x10 ³

~~(1) All values reported in mg/l unless otherwise specified.~~







The Thorburg Reference

United States Patent

(11) 3,617,554

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 Succasunna, N.J.
 [21] Appl. No. 42,794
 [22] Filed June 2, 1970
 Division of Ser. No. 744,076, July 11, 1968
 [45] Patented Nov. 2, 1971
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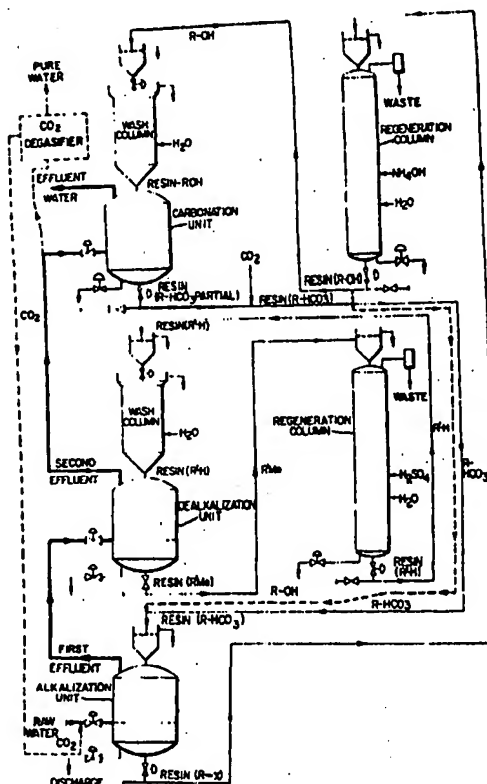
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 Primary Examiner—Samih N. Zaharna
 Attorney—Browdy and Neimark

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[54] **DESALTING AND PURIFYING WATER BY CONTINUOUS ION EXCHANGE**
 5 Claims, 1 Drawing Fig.

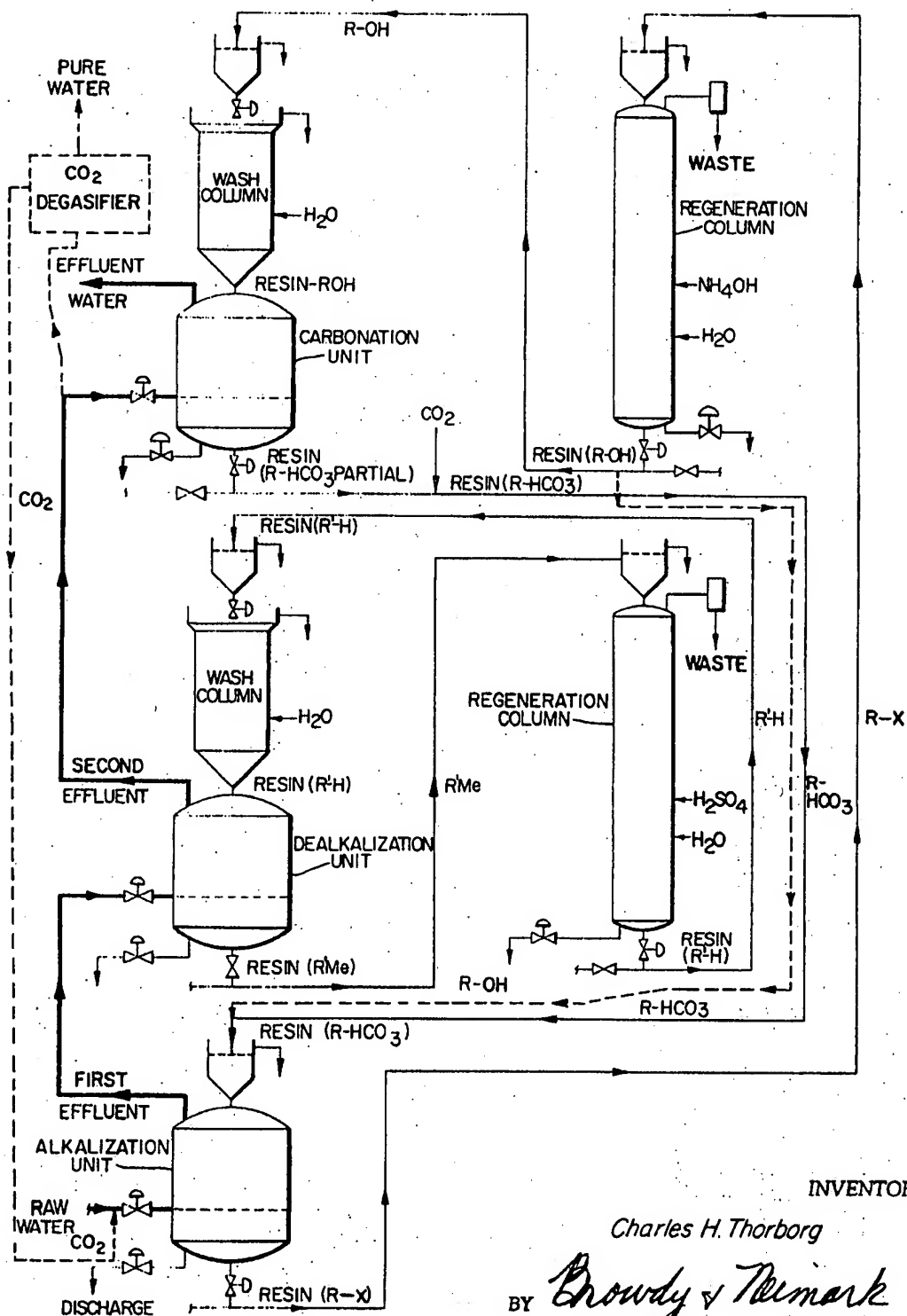
[52] U.S. Cl. 210/26,
 210/33
 [51] Int. Cl. B01d 15/02,
 B01d 15/06
 [50] Field of Search 210/26, 32,
 33, 37, 38

ABSTRACT: A method and apparatus are provided for the continuous treatment of brackish water, sea water, industrial wastes or sewage effluents using continuous ion exchange. Three units are provided in series, the raw water entering the first unit and purified water leaving the third unit. While the water moves continuously through the three units, an ion exchange resin is caused to flow countercurrent therethrough, exchange resin is caused to flow countercurrent therethrough, a weak base anion exchange resin in the bicarbonate state passing through the first unit and the same resin, in the free base form, passing through the third unit. Passing through the second unit countercurrent to the effluent is a weak acid cation exchange resin. After passage through the first and second units, the resins are regenerated. The third unit is a carbon dioxide degasifier.



PATENTED NOV 2 1971

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DESALTING AND PURIFYING WATER BY CONTINUOUS ION EXCHANGE

The present application is a division of copending application Ser. No. 744,076 filed July 11, 1968.

The present invention relates to a method and apparatus for desalting and purifying water by continuous ion exchange and, more particularly, to a desalination process for the treatment of brackish water, sea water, industrial wastes and sewage effluents utilizing continuous countercurrent treatment with weak base anion exchange resin and a weak acid cation exchange resin.

The desalination of salt-containing impure water has received a great deal of attention because of the overwhelming world need of fresh water. Prior art developments have been carried out in the fields of distillation, freezing, the use of semipermeable membranes, extraction procedures, ion exchange and combinations of these various procedures.

In recent years, the use of ion exchange for the purification of brackish waters in particular has been advanced by the development and utilization of weak base anion exchange resins and weak acid cation exchange resins. Prior to use of these resins it was found that ion exchange of brackish waters utilizing conventional ion exchange resins was prohibitively expensive due to the large proportion of dissolved solids in brackish water and the limiting factor in the use of conventional ion exchange resins because the cost of regenerant for such resins increased proportionately with the increase in salinity. The great advantage in the weak acid and weak base exchange resins lies in the low cost of their regeneration and their very high efficiency.

However, in spite of the advantages which have been provided in the utilization of such weak base and weak acid ion exchange resins in the desalination of brackish waters, a number of problems have remained. Thus, the cyclic procedures in which these resins have been utilized involve complex piping arrangements which take up excessive factory space and involve high initial cost, and their operation utilizes excessive chemical consumption. In addition, these cyclic operations do not achieve maximum efficiency with respect to the economical removal of solids from the waters treated. In addition, these cyclic operations have used excessive quantities of carbon dioxide for conversion of the weak base anion exchange resins to the bicarbonate form; and have also utilized an excessive volume of wasted water.

It is, accordingly, an object of the present invention to overcome and/or reduce the deficiencies inherent in the prior art, such as indicated above.

It is another object of the present invention to provide a new, unobvious and more efficient system of desalination utilizing ion exchange.

It is another object of the present invention to provide for the continuous, countercurrent ion exchange desalination of ion-containing waters.

It is another object of the present invention to use countercurrent exchange both in treatment and in regeneration to improve the efficiency of maximum solid removal from salt-containing water, thereby increasing economy.

It is another object of the present invention to reduce chemical consumption in the removal of ions from salt-containing water.

It is another object of the present invention to reduce the makeup of carbon dioxide as the continuous ion exchange process completely exhausts the resin, thus allowing almost complete conversion to the bicarbonate form in the carbonation column.

It is another object of the present invention to reduce the floorspace required in a desalination system without reducing the efficiency.

It is another object of the present invention to reduce the size of reaction vessels due to the use of high flow velocities utilized in the continuous ion exchange of the present invention.

It is another object of the present invention to greatly simplify the piping arrangement normally required in ion exchange apparatus utilizing weak base anion exchange resins.

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It is another object of the present invention to reduce the volume of water wasted as compared to known systems.

It is yet another object of the present invention to reduce the equipment installation costs by providing simplified structure.

These and other objects in the nature and advantages of the instant invention will be more apparent from the following detailed description of the invention taken in conjunction with the drawing which shows a flow diagram of an embodiment of the present invention.

Briefly, raw water, such as brackish water, is fed continuously to the bottom of an alkalization unit which receives at the top thereof continuously and countercurrent to the flow of such water a weak anion exchange resin in the bicarbonate form $R-HCO_3$. The resin exchanges raw water anions for bicarbonate. The resin leaves the unit at the bottom thereof in the salt form $R-X$ (i.e. chloride, sulfate, nitrate, etc.) equal to the raw water analysis while the water, designated first effluent leaves the top of the alkalization unit containing bicarbonate impurities (calcium bicarbonate, magnesium bicarbonate, etc.). The resin $R-X$ leaving the bottom of the alkalization unit is transferred to a regeneration column where it is converted to its free base form with a suitable regenerant, such as ammonia, lime, etc.

In the meantime, the water or first effluent is passed upwardly from the alkalization unit to the bottom of the dealkalinization unit which is charged at its upper end with a weak acid cation exchange resin in the hydrogen form $R'-H$. The resin flowing continuously downwardly countercurrent to the upward flow of the effluent exchanges the cations therein for hydrogen. The released hydrogen reacts with the bicarbonate present thereby leaving pure water and carbon dioxide (plus any slippage of ions through the resins). The resin leaves the bottom of the dealkalinization unit in the metal form $R'-Me$ (containing calcium, magnesium sodium etc.) and is transferred to a regeneration column where it is converted countercurrently back to the hydrogen form $R'-H$ with a suitable acid regenerant such as sulfuric acid. The resin is then again recycled to the top of the dealkalinization unit.

The second effluent comprising pure water and carbon dioxide leaving the top of the dealkalinization unit is then passed to the bottom of a carbonation unit through which such effluent flows countercurrent to the weak base anion exchange resin in its free base form $R-OH$ which is fed to the top of the carbonation unit. The resin in its free base form is converted to the bicarbonate form $R-HCO_3$ by the carbon dioxide present in the effluent, and such converted resin is then passed from the bottom of the carbonation unit to the top of the alkalization unit as previously described. Any required makeup of carbon dioxide needed to complete carbonation of the weak base anion exchange resin is added during the transfer of the resin from the carbonation unit to the alkalization unit. The water leaves the top of the carbonation unit suitable for most uses such as drinking, industrial uses, irrigation, etc.; if desired, however, the water may be then passed to a further polishing zone to provide ultra-pure water.

As will be apparent from the flow diagram, it is advantageous to wash the ion exchange resins prior to feeding thereof to the carbonation unit and the dealkalinization unit. This and other details of operation including relative flow rates, etc. will be readily apparent to those having normal skill in the art.

The preferred ion exchange resins used in the present invention are manufactured by Rohm and Haas and are sold under the trade names "Amberlite IRA-68" (the weak base anion exchange resin) and "Amberlite IRC-84" (the weak acid cation exchange resin). "Amberlite IRA-68" is a synthetic resin provided in spherical bead form of 16-50 U.S. Standard Mesh having a weight of 46 pounds per cubic foot and containing tertiary amine functional groups. "Amberlite IRC-84" is a carboxylic cation exchange resin provided as spherical particles of 16-50 U.S. Standard Mesh and having a weight of 47 pounds per cubic foot. While these two commercially available ion exchange resins are preferred, it will be understood

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that other resins, having similar properties, may be used in that place. A number of other weak base anion exchange resins and weak acid cation exchange resins are presently commercially available; one such weak acid cation exchange resin is "Zerolit 216" which is a condensation production containing both phenolic and carboxylic groups. Another weak acid cation exchange resin is "Amberlite IRC-50."

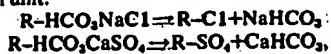
While the present invention has been described with respect to a three-column system, it will be understood that the present invention may be utilized preferably with six columns, and may be utilized with as few as only two columns together with a carbon dioxide degasifier.

The present invention and its advantages will be better understood by reference to the following operative examples, which it is understood are not limitative but are merely exemplary:

EXAMPLE I

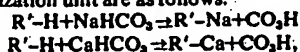
A three absorption column system such as shown in the FIGURE is utilized. The weak base anion exchange resin used is "Amberlite IRA-68." The raw water fed to the alkalization unit (the first column) is brackish water containing sodium, calcium and magnesium anions and chloride, sulfate and carbonate cations.

The following reactions typify the reactions occurring in the alkalization unit:



wherein R signifies the weak base anion exchange resin.

The effluent passing from the alkalization unit to the dealkalinization unit contains sodium bicarbonate, calcium bicarbonate and magnesium bicarbonate. This effluent is fed to the bottom of the dealkalinization unit while, countercurrent therewith, "Amberlite IRC-84" in hydrogen form is fed to the top of the dealkalinization unit. The typical reactions occurring in the dealkalinization unit are as follows:



wherein R' signifies the weak acid cation exchange resin.

The effluent passing from the dealkalinization unit to the bottom of the carbonation unit contains CO_2H . The "Amberlite IRA-68" is fed to the top of the carbonation unit in its free base form and the reaction occurring is:



The weak base anion exchange resin fed to the top of the alkalization unit from the bottom of the carbonation unit is signified by the formula R-HCO_3 . After treatment in the alkalization unit, the unregenerated resin is signified by the formula R-X , e.g. R-Cl or R-SO_4 . After regeneration with a suitable regenerant such as sodium hydroxide or calcium hydroxide, but preferably ammonia, the weak base anion exchange resin as it is fed to the top of the carbonation unit has the empirical formula R-OH . In the above formula, R signifies the weak base anion exchange resin and X signifies the exchangeable anionic material including chloride, sulfate and nitrate.

The weak acid cation exchange resin is fed to the top of the dealkalinization unit in its free acid form and is designated by the formula R'H . This resin leaves the bottom of the dealkalinization unit in accordance with the formula R'Me and, after regeneration with a suitable reagent such as sulfuric acid, hydrochloric acid, nitric acid or sulfurous acid, is reconverted to the free acid form as signified by the formula R'H . In the above formula R' signifies the weak acid cation exchange resin and Me signifies the metal cation, such as sodium and calcium.

In the present example, the flow of effluent, various reagents and ion exchange resins are as shown in the FIGURE.

The desalination of brackish water according to the example is economical because of the following factors. The resin regeneration is close to the theoretical (stoichiometric) efficiency with low chemical cost and negligible waste problems because very little excess regenerant is necessary; the ion

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exchange capacity of the resins is high, thereby necessitating only a low resin investment; there is a minimum water loss for the regeneration operations; and there is a minimal waste disposal problem because the continuous regeneration results in a continuous neutralization of excess regenerant.

EXAMPLE 2

In this procedure only two adsorption columns are used, namely the alkalization unit and the dealkalinization unit, together with a CO_2 degasifier shown in phantom in the FIGURE. In this system, carbon dioxide, either fresh or that recovered from the degasifier, is added directly to the raw water, as shown by the dash line in the FIGURE, before it is fed to the alkalization unit. The exhausted weak base anion exchange resin leaving the bottom of the alkalization unit is regenerated with ammonia and is returned directly to the top of the alkalization unit as shown by the dash line in the FIGURE. The dealkalinization unit is operated as described above. The basic difference is that the first unit combines the functions of the alkalization unit and the carbonation unit so that both reactions occur in this unit.

The foregoing description of the specific embodiments will so fully reveal the general nature of the invention that others can, by applying current knowledge, readily modify such specific embodiments and/or adapt them for various applications without departing from the generic concept and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the following claims.

What is claimed is:

1. A Method of desalting water comprising

1. Continuously adding carbon dioxide to raw water;

2. continuously passing said raw water containing carbon dioxide countercurrent to a weak base anion exchange resin represented by the formula R-OH , wherein R is the resin, to yield a first effluent containing alkali metal and alkaline earth metal bicarbonates;

3. continuously passing said first effluent countercurrent to a weak acid cation exchange resin represented by the formula R'-H , wherein R' is the resin, to yield a second effluent containing carbon dioxide;

4. continuously passing the contaminated weak anion exchange resin from step two, now represented by the formula R-X wherein X is an anionic impurity, to a regeneration zone, introducing basic regenerant to said zone and thereby continuously regenerating said resin to the R-OH form and returning said resin to step two;

5. continuously passing said second effluent from step three to a carbon dioxide degasifier, thereby obtaining pure water and also recovering carbon dioxide;

6. continuously passing the contaminated weak acid cation exchange resin from step three to a regeneration zone, introducing acidic regenerant to said zone and thereby continuously regenerating said cation exchange resin; and recycling said cation exchange resin to step three; and

7. recycling carbon dioxide recovered in step five to step one.

2. Apparatus for carrying out the desalting of water comprising

means to feed carbon dioxide continuously to raw water;

a combined alkalization and carbonation unit for removing anions from raw water, means to continuously feed said raw water and carbon dioxide to said alkalization and carbonation unit, means to continuously feed weak base anion exchange resin in hydroxyl form to said alkalization and carbonation unit countercurrent to the water flow, means to continuously discharge contaminated anion exchange resin from said alkalization and carbonation unit, and means to continuously discharge a first effluent from said alkalization and carbonation unit;

a dealkalinization unit for receiving said first effluent from said alkalization and carbonation unit and for removing

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cations from said first effluent to provide a second effluent, means to continuously feed weak acid cation exchange resin in hydrogen form through said dealkalization unit countercurrent to the effluent flow, means to continuously regenerate contaminated weak acid cation exchange resin to provide said resin in hydrogen form, means to continuously pass contaminated weak acid ion exchange resin to said cation regenerating means, means to pass said regenerated weak acid cation exchange resin in hydrogen form from said regenerating means back to said dealkalization unit, and means to continuously discharge said second effluent from said dealkalization unit;
a degasifier for receiving said second effluent from said dealkalization unit and removing the carbon dioxide from said second effluent;
an anion exchange resin regenerating means, means to

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supply regenerant to said anion resin regenerating means, means to pass contaminated anion exchange resin from said alkalization and carbonation unit to said anion resin regenerating means, and means for passing regenerated anion exchange resin in hydroxyl form to said alkalization and carbonation unit; and
means to recycle carbon dioxide from said degasifier to said carbon dioxide feeding means.

3. A process in accordance with claim 1 wherein said basic regenerant in step (4) comprises NH_4OH .

4. A process in accordance with claim 1 wherein said acidic regenerant used in step (6) comprises H_2SO_4 .

5. A process in accordance with claim 1 wherein said resins flow downwardly and said raw water and first effluent flow upwardly in said countercurrent steps (2) and (3).

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